Reprinted from

Applied Physics Letters

Volume 66 9 January 1995 Number 2

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(Received 27 July 1994; accepted for publication 4 November 1994)

pp. 242-244

a publication of the American Institute of Physics

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Stable secondary electron emission from cesium terminated chemical vapor deposited (CVD) diamond films has been observed. Total secondary yield coefficients (σ) ranged from 25 to 50 and were stable under continuous exposure to an electron beam from targets tested for up to 170 h. Primary current densities ranged from 1.5 to 50.0 mA/cm^2. Targets were coated with CsI from 10 to 100 nm thick. Auger electron spectroscopy was used to show that the emission was activated by electron beam induced iodine depletion after short beam exposures, leaving a Cs terminated diamond surface independent of the initial CsI thickness. The electron beam activated-alkali terminated surface is air stable and stable during heating in vacuum up to 120 °C. This behavior has also been observed from CVD diamond coated with CsF, KCl, and NaCl. © *1995 American Institute of Physics.*

Chemical vapor deposited (CVD) diamond is promising for novel electronic applications due to its heat dissipative properties, negative electron affinity,[1] and its relative ease of fabrication.[2] High secondary electron emission (SEE) properties, σ=12–48, have been measured from CVD diamond terminated with hydrogen,[3–5] which is up to 20 times greater than σ from materials presently used in secondary emitter applications.[6,7] The problems encountered using diamond as a secondary emitter are the instability of σ under electron beam exposure due to the desorption of hydrogen from the surface, and graphitization of the diamond surface due to ion bombardment.[4] The high σ is stable under continuous electron beam exposure in a hydrogen environment if the ratio of hydrogen molecules to electrons impinging upon the surface is approximately 1:1 or greater.[3,4]

Alkali-halides are known for electron transport and emission enhancing properties.[8–10] CsI has been used quite successfully as a photocathode in multichannel plate electron multipliers resulting in improved sensitivity.[11] The major drawback of using thick alkali-halide coatings in electron beam applications is their insulating property. However, thin alkali-halide films can be conducting. The purpose of this work was to investigate the possibility of stabilizing the SEE properties of CVD diamond by vacuum depositing thin alkali-halide films onto the surface.

The test samples used in this work were polycrystalline diamond films on Mo substrates grown by microwave plasma and hot filament assisted CVD. CsI, KCl, CsF, and NaCl films, 10–100 nm thick, were vapor deposited onto the diamond targets. This work will concentrate on the CsI coated samples. SEE measurements were made on each target before and after the alkali-halide depositions. The experimental setup has been described in detail elsewhere.[4] σ versus time (fluence) was measured from the CsI coated diamond films at room temperature and at temperatures up to 160 °C. The targets were exposed to the electron beam at current densities of 1.5–50.0 mA/cm^2, in a primary beam energy range of 1.0–1.5 keV, for durations of 6–170 h. The current density and primary beam energy were held constant during each exposure. σ versus time (fluence) and energy was measured from CsI and KCl films on Mo substrates, in the same thickness range as grown on the diamond films, for comparison. Measurements of σ versus time (fluence) were also made from CVD diamond films coated with CsF, KCl, and NaCl.

The SEE properties from clean CVD diamond (hydrogen terminated) targets have been described in detail,[3–5] and the uncoated diamond samples used in this work behaved as those targets measured previously. Maximum values of σ from the as-received, uncoated targets ranged from 6 to 12 and occurred at a beam energy of 1 keV. Figure 1 shows σ versus energy from a representative target before and after a 10 nm CsI coating was deposited. For the coated sample, the data were collected after the surface was activated by electron exposure. The target was negatively biased to eliminate space charge effects.

Figure 2 shows σ versus time from a 100 nm thick CsI film on Mo, and from a diamond target before and after a 10 nm thick CsI film was deposited. The data were collected while the samples were under continuous electron bombardment. CsI coatings on both diamond and Mo were initially unstable under exposure to the electron beam. All data were collected using a primary current density of 15 mA/cm^2 at 1500 eV. σ from the uncoated diamond films typically degraded to a value of ~3 due to electron beam induced desorption of hydrogen.[4] σ from the CsI and KCl coated dia-

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 0003-6951/95/66(2)/242/3/$6.00

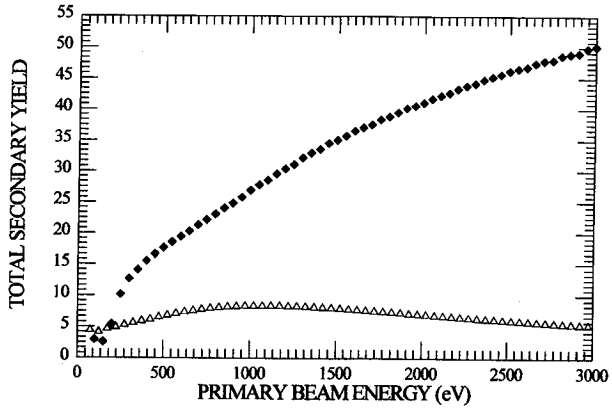

FIG. 1. σ vs primary beam energy from a representative CVD diamond target before (△) and after (◆) deposition of a 10 nm thick CsI surface layer. The data from the coated sample were taken after the surface was activated by electron exposure.

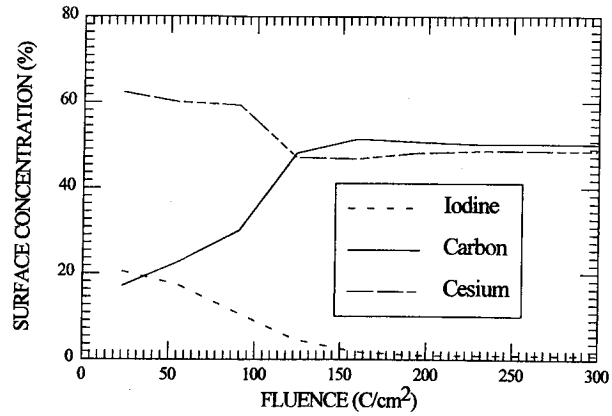

FIG. 3. Surface concentration vs time (fluence) from CVD diamond films coated with 100 nm of CsI. The surface was activated by electron induced depletion of the iodine, and the remaining Cs termination was independent of the initial CsI thickness.

mond films invariably degraded from the as-received values of 8–12 to values as low as 1.5 at the onset of electron exposure, then rose above the initial values after fluences on the order of 10 C/cm^2. σ from the CsI-coated diamond samples showed no signs of degradation after the initial activation. σ from the coated sample shown in Fig. 2 increased steadily until it stabilized at a value of 22 after 67 h. The yield remained stable for the next 103 h, at which time the test was terminated. All CsI-coated samples showed the same stable emission, independent of the initial thickness of the CsI coating. SEE behavior similar to this was observed previously from a diamond/Mo sample which is now known to have been contaminated with NaCl.[12]

Auger electron spectroscopy (AES) from the CsI-coated films showed that continuous electron beam exposure depleted the iodine after relatively low fluences, as low as ~50 C/cm^2 for the 10 nm thick coatings and 150 C/cm^2 for the 100 nm thick coatings, leaving a Cs-rich diamond surface which is correlated with the high stable σ as is illustrated in Fig. 3. These electron beam activated-alkali terminated (EBAAT) diamond films exhibited stable emission in every case, after depletion of the halogen. The fluence required to activate the stable emission was dependent on the initial thicknesses of the alkali-halide films. The final concentration of Cs after the process of activation was independent of the initial CsI thickness. In the case of pure CsI on Mo, AES showed that the film was also depleted of iodine due to the electron beam exposure, however, σ saturated at a value of 3, as is seen in Fig. 2.

AES showed that the electron beam depleted the chlorine from the KCl-coated diamond samples, leaving the surface terminated with potassium. The fluence required to achieve this was ~500 C/cm^2, which was much greater than required to deplete the iodine from the CsI-coated films.

We observed that values at which σ stabilized after electron exposure had an inverse dependence on the primary current density. σ stabilized at values between 28 and 30 when exposed to 1.90 mA/cm^2, and 6–10 when exposed to 50

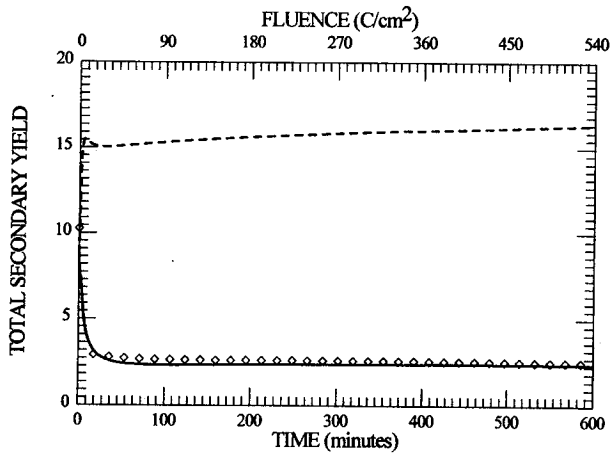

FIG. 2. σ vs time (fluence) from a representative CVD diamond target before (◇) and after (dashed line) deposition of a 10 nm thick CsI surface layer. σ from a 100 nm thick CsI film on Mo (solid line) is included for comparison.

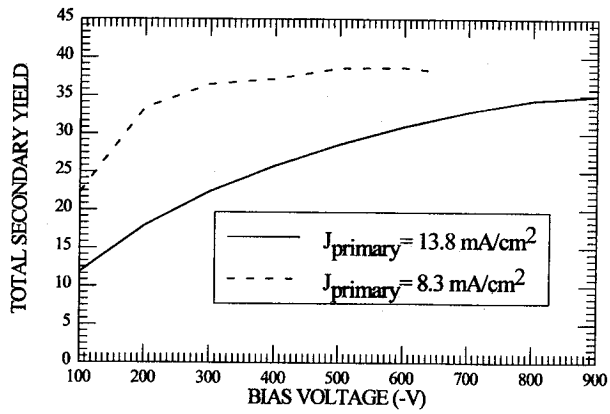

FIG. 4. σ vs target bias voltage from an EBAAT diamond film which was initially coated with 10 nm CsI. The increase in σ with increased negative potential on the target strongly suggests that space charge is limiting the secondary emission at higher primary current densities.

mA/cm^2. Figure 4 shows the maximum value of σ as a function of target bias for two primary current densities at a fixed primary beam energy of 1500 eV. σ approached the same maximum value independent of current density at high bias voltages which suggests that space charge may have been impeding the SEE at high primary current densities. Two 80% transparent grids were mounted, 1 and 2 mm, respectively, above and parallel to the target surface for space charge dissipation. With a field of 250 V/mm, we were able to measure a total secondary yield of ~35 at 1500 eV, independent of the primary current density.

Targets were removed from the vacuum chamber and exposed to air at room temperature for 1 week, and the retested. Short exposure to the electron beam (<1 C/cm^2) was necessary for the previously exposed regions to regain the same high stable σ. This was probably the result of desorption of surface contaminants induced by the electron beam. AES, in these regions, showed no oxygen contamination after short electron beam exposures.

Under exposure to a 12 mA/cm^2 primary beam current while heating at 160 °C, σ rose to 38, then degraded to 3 in a 72 h period. However σ was stable under the same current density while heating to 120 °C during a 72 h test.

Targets coated with KCl, NaCl, and CsF all showed the same SEE behavior, with σ ranging from 12 to 40 depending on the specific target. These EBAAT CVD diamond films represent a material capable of sustaining very high secondary yields under practical electron device operating conditions.

In summary, high stable SEE from EBAAT CVD diamond films has been observed. The surface was activated by exposure to an electron beam which desorbed the halogen and left a thin alkali metal termination of the diamond surface, independent of the initial thickness of the alkali-halide coating. There was no indication of degradation of σ due to electron exposure once the surface was activated. This behavior has been observed from CVD diamond films coated with CsI, KCl, NaCl, and CsF, suggesting that any alkali-halide may provide a similar effect and should be investigated.

A material with such high stable secondary yield can be used to construct an electron amplifier with gain several orders of magnitude higher than is presently attainable. Materials which are good secondary emitters can be potentially good photoemitters as well, provided the photons are of sufficient energy to excite secondary electrons into the conduction band. Thus, the CsI-coated diamond may be used as the photocathode in a PMT significantly improving the sensitivity and gain. Vacuum electronic devices that depend upon secondary emission, such as crossed field amplifiers and magnetron oscillators, may exhibit significant improvement by implementing a very high secondary yield material as a cold cathode. The availability of stable, high yield secondary electron emitters may enable the development of novel vacuum electronic devices.

The authors would like to thank Louis Maschak, and Ben Ebihara for assisting with the experimental setup. They would also like to thank R. Ramesham and M. F. Rose of the Space Power Institute at Auburn University for providing some of the CVD diamond targets, and Sharon Austin of Fermi Lab for performing the alkali-halide depositions. This work was supported by The National Research Council and NASA Lewis Research Center.

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